U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-262 522

Conventional Tertiary Treatment

District of Columbia Dept of Environmental Services, Washington

Prepared for

Municipai Environmental Research Lab, Cincinnati, Ohio Wastewater Research Div

Nov 76

019078

PB 262 522

EPA-600/2-76-251
November 1976

Environmental Protection Technology Series

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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-76-251		

4. TITLE AND SUBTITLE
Conventional Tertiary Treatment

5. REPORT DATE
November 1976 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Government of the District of Columbia
EPA-DC Pilot Plant
5000 Overlook Ave. SW
Washington, D.C. 20032

10. PROGRAM ELEMENT NO.
1BC611

11. CONTRACT/GRANT NO.
14-12-818

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES
*Presently with MERL, Cincinnati

16. ABSTRACT

Tertiary treatment on effluent from the EPA-DC Pilot Plant's step aeration activated sludge system included two-stage or single-stage lime clarification, air stripping of ammonia, dual-media filtration, neutralization, and activated carbon adsorption. With a good secondary effluent to the lime clarification units and the dual-media filtration system, the two-stage process produced residual BOD and phosphorus (as P) concentrations of 1.4 mg/l and 0.09 mg/l, respectively. With fresh carbon, the TOC was less than 3 mg/l after treatment by carbon adsorption. Single-stage operation with sodium carbonate addition and with a good quality secondary effluent as feed produced an average phosphorus residual of 0.53 mg/l as P after clarification. Following dual-media filtration, the phosphorus residual as P was reduced to 0.10 mg/l. With a poor quality secondary effluent (filamentous growth), the slurry pool in the first-stage solid contactor unit was unstable and produced lower quality effluents. At warm air temperatures (greater than 75°F), 80 percent of the ammonia was air stripped from the effluent of the two-stage lime system. Recalcined lime was recycled to the clarification system without a reduction in the efficiency of the tertiary system.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Sewage Treatment	*Filtration	Two-stage lime clarification	13B
Calcium oxide	*Activated carbon	Lime reuse	
Calcium phosphates	Ammonia	Phosphorus removal	
*Clarification		*Tertiary treatment ammonia stripping	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	43
	20. SECURITY CLASS (This page) Unclassified	22. PRICE 4.00

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1976-757-056/5433 Region No. 5-11

EPA-600/2-76-251
November 1976

CONVENTIONAL TERTIARY TREATMENT

by

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Contract Number 14-12-818

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report describes pilot testing of physical-chemical treatment for the reduction of residual pollutants in secondary effluent. The residual nutrients and organic materials are efficiently removed to low levels to prevent accelerated eutrophication.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

EXECUTIVE SUMMARY

The objective was to evaluate conventional-tertiary treatment consisting of primary sedimentation, step aeration, two-stage or single-stage (lime-sodium carbonate) high pH lime clarification, ammonia stripping, filtration, neutralization, and activated carbon adsorption for potential application as an AWT Plant in the District of Columbia.

The secondary effluent from the EPA-DC Pilot Plant's step aeration process was fed, usually with an average flow of 58,000 gpd and a diurnal variation of 33,000 to 100,000 gpd, to a physical-chemical treatment system consisting of either one or two lime treatment solids contactors (with a recarbonation tank in the two-stage operation), an air cooling tower (for ammonia stripping), dual-media filter, a neutralization tank and a small activated carbon column (laboratory pilot scale - 0.32 gpm flow). Each clarifier was divided into 4 zones; a primary mixing zone (rapid mix), a secondary zone (flocculation), a clarification zone and a sludge densification zone. Solids from the densification zone from each clarifier were externally recycled at 10 percent of average flow to either the primary mixing zone or to the recarbonation tank. The clarification system was designed for a maximum flow of 100,000 gal/day with a maximum overflow rate of 2,000 gal/day/ft^2. The system was usually operated on a diurnal cycle with a maximum to minimum flow rate of about 3:1.

During the two-stage clarification operation, the pH was reduced to approximately 10.5 in the recarbonation tank where the average contact time was 15 minutes. Five mg/l of ferric ions were added to the primary mixing zone of the second clarifier to improve the flocculation of the precipitation column carbonate. Single-stage operation consisted of pumping sodium carbonate solution to either the primary or secondary mixing zone of the first clarifier to precipitate the excess column ions. The recarbonation tank and second-stage clarifier were eliminated.

Ammonia air stripping was applied to the second-stage clarifier effluent at pH 10.5. The stripping system included five crossflow cooling towers, each packed with polyproplylene grids. The water was pumped to a distribution box located on the top of each tower and flowed downward over the grids. The air was drawn countercurrent to the flow of water, between towers and crossflow within the packing of each tower.

The filtration system consisted of a splitter box followed by two gravity fed dual-media filters. The filters were backwashed for 10 minutes by a sequential surface-wash backwash system. The flows of the surface-wash and backwash system were 3 and 20 gal/min/ft^2, respectively.

A side stream of the filtered effluent was neutralized to pH 7-8 and pumped through four 3-inch activated carbon adsorption columns. At a constant rate of 0.32 gal.min, the loading to the column was 7 gal/min/ft^2 with a total empty bed contact time of 30 minutes. The columns were manually backwashed every day at a rate of 15 gpm/ft^2.

While the tertiary treatment demonstrated excellent removals of phosphorus and organic carbon, the nitrogen removal by ammonia stripping was not satisfactory for the District of Columbia treatment requirements because of air temperature effects on the stripping process. Specifically, two-stage lime precipitation of a good quality step aeration effluent in the solids contactor units produced low residuals of 0.13 mg/1 of phosphorus and 2.1 mg/1 of BOD. Dual-media filtration of the chemically clarified effluent reduced phosphorus and BOD concentrations to 0.09 mg/1 P and 1.4 mg/1, respectively.

Single-stage clarification (ph 11.5, sodium carbonate addition) with a good quality secondary effluent produced a phosphorus residual of 0.53 mg/1 as P in the clarified effluent. The carryover precipitated phosphorus, however, was filterable as filtration produced an effluent with an average residual phosphorus concentration of 0.10 mg/1 P. Operational difficulties in the pumping of sodium carbonate solution produced a carryover of excess soluble calcium ion into the filter. The post precipitation of these ions as $CaCO_3$ in the filters caused cementation and channeling of the filter.

Recalcined lime, with recoveries up to 75% of the total solids slurry, was recycled to the clarification system without a loss in efficiency of the tertiary system. With filamentous growths in the activated sludge system, high organic solids concentrations entered the first-stage clarifier, produced slurry pool instability and reduced the treatment efficiency of the system.

In the ammonia stripping studies with inlet water and air temperatures of 25°C (77°F) and 24.4°C (76°F), respectively and an air to liquid rate of 327 ft^3 air/gallon liquid, 80 percent of the available ammonia was air stripped from the effluent for the two-stage lime system at pH 10.5. A reduction in inlet air temperature to 6°C (43°F) reduced the removal effiency to 56 percent. At pH 10.5, the calcium carbonate scale rate was 16 mg/1 $CaCO_3$. Activated carbon adsorption removed 55 percent of the total organic carbon from the neutralized filter effluent with an average residual of 3.7 mg/1.

The results on the District of Columbia wastewater further confirm earlier work on the treatment capability and reliability of tertiary physical-chemical treatment for the removal of phosphorus and carbon. The work also demonstrated the limitations of ammonia stripping for nitrogen removal. The design data, the operating experiences, and the process limitations are thus valuable in the area of production of high quality water for very high water pollution control standards and for water reuse.

This report was submitted in partial fulfillment of Contract No. 14-12-818, by the Department of Environmental Services, Government of the District of Columbia, under the sponsership of the Office of Research and Development, U.S. Environmental Protection Agency. Work was completed as of October 1971.

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ACKNOWLEDGMENTS

The pilot system was constructed, maintained and operated by the EPA-DC pilot plant staff under the direction of Robert A. Hallbrook, chief mechanic; Walter W. Schuk, chief instrument technician; George D. Gray, chief operator; and Howard P. Warner, chief analytical chemist. Alan B. Hais maintained and operated the carbon adsorption system.

SECTION I

INTRODUCTION

As a result of the Potomac River-Washington Metropolitan Area Enforcement Conference, 1969 (1) the District of Columbia's Water Pollution Control Plant was required to attain high removals of carbon, phosphorus and nitrogen prior to discharge to the Potomac River. To meet these requirements, various treatment systems for the removal of C, P and N were studied at the EPA-DC Pilot Plant in Washington, D. C. One of the systems studied consisted of primary, secondary and tertiary (physical-chemical) treatment and is described as conventional-tertiary treatment.

Tertiary treatment has been applied to secondary wastewaters for the removal of phosphorus, nitrogen and organic carbon (2)(3)(4)(5)(6), and usually includes the following unit processes: chemical clarification (alum, iron or lime), filtration, ammonia removal (ion exchange, breakpoint chlorination or air stripping) and activated carbon adsorption. Lime precipitation has generally been selected, over use of alum and iron salts, as the prime chemical clarification process since it produces a treatable sludge with a high pH which can be used in conjunction with ammonia air stripping. Alternate methods of chemical precipitation have been used depending on the relative hardness of the wastewater and on the relative phosphorous removal required. A high pH (~ 11.5) lime process with one or two-stages is generally applied to waters of moderate alkalinities (100-200 mg/l $CaCO_3$), while in areas of higher alkalinities (~ 250 mg/l $CaCO_3$), a low pH (~ 9.5) single-stage system may be used. The high pH (~ 11.5) operation produces water from which ammonia may be air stripped (7). Experimental studies reveal that phosphorus residuals of less than 0.2 mg/l as P (8) have been obtained with the high pH lime process while residuals in the vicinity of 0.5 mg/l as P (9) are typical with the low pH process.

In the high pH lime process, lime is added to the wastewater to increase the pH above 11.5 and to precipitate the bicarbonate, phosphorus and magnesium ions according to the following reactions.

$$Ca^{++} + HCO_3^- + OH^- \rightarrow \underline{CaCO_3} + H_2O \qquad (1)$$

$$5Ca^{++} + 3H_2PO_4^- + 7OH^- \rightarrow \underline{Ca_5OH(PO_4)_3} + 6H_2O \qquad (2)$$

$$Mg^{++} + 2OH^- \rightarrow \underline{Mg(OH)_2} \qquad (3)$$

The magnesium hydroxide formed is an excellent coagulant aid and flocculates the organic solids and the precipitated inorganic solids. However, the amount of lime required to attain pH 11.5 produces an excess of calcium ions in the wastewater. Two methods can be used for the removal of the calcium ions. One consists of recarbonation of the first-stage clarified effluent to pH 9.5-10.5 with carbon dioxide to precipitate the excess ions as calcium carbonate according to Equation 4. This precipitation is settled in the second-stage clarifier. Alternately the addition of sodium carbonate into the first-stage clarifier can be used to precipitate the calcium ions as calcium carbonate without requiring a second sedimentation stage. This reaction is described by Equation 5.

$$Ca^{++} + 2OH^{-} + CO_2 \rightarrow \underline{CaCO_3} + H_2O \qquad (4)$$

$$Ca^{++} + 2Na^{+} + CO_3^{=} \rightarrow CaCO_3 + 2Na^{+} \qquad (5)$$

Thus the high lime process has two basic modes of operation, single-stage sedimentation with sodium carbonate addition and two-stage sedimentation with carbon dioxide addition between the stages. In either the single or the two-stage system, the effluents may be neutralized by additional carbon dioxide as shown in Equation 6.

$$OH^{-} + CO_2 \rightarrow HCO_3^{-} \qquad (6)$$

In the low pH system, lime is added to increase the pH to approximately 9.5 and precipitate a portion of the bicarbonate ions (Equation 1) as calcium carbonate and most of the phosphate (Equation 2). The magnesium ions generally are not precipitated. Calcium ions are not in excess and recarbonation is not required unless neutralization of the effluent is desired. The sludge produced during any of the lime precipitation processes is thickened, dewatered and fed to furnaces for recalcination. The recalcined lime is returned to the system while the stack gas containing approximately 10 percent carbon dioxide is used for recarbonation and neutralization.

Following chemical clarification, filtration is applied for additional solids and phosphorus removal. Mixed bed filtration (sand and coal, or garnet, sand and coal) has been successfully applied to lime treated secondary effluents. To prevent the possibility of calcium carbonate scale within the media, the clarified effluent should be neutralized to less than pH 8 prior to filtration.

Three methods are available for removal of nitrogen by tertiary treatment and are: breakpoint chlorination, selective ion exchange and air stripping

of the ammonia. All of these processes remove nitrogen only in the form of ammonia, and therefore, in the tertiary mode must be applied to a non-nitrified secondary effluent. Breakpoint chlorination requires contacting a neutralized or non-neutralized filtered effluent in a highly mixed, pH controlled system with chlorine at a chlorine to nitrogen ratio of approximately 9:1 Cl:N (10). Selective ion exchange is applied to a neutralized filter effluent for ammonia removal in packed bed pressurized control units containing a natural zeolite, clinoptilolite, which is selective for the ammonium ion (10).

Air stripping of ammonia (2)(4) is used in conjunction with the lime precipitation process which raises the pH and converts the ammonium ion to ammonia according to the following equation:

$$NH_4 + OH \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O \qquad (7)$$

Unfortunately, ammonia is highly soluble in water, and its volatility decreases markedly with decreasing temperature. As a result, effective air stripping requires warm temperatures and the use of large volumes of air per unit volume of water.

For the removal of soluble organic carbon in tertiary treatment systems, filtered effluents have been applied to activated carbon systems operating as packed bed downflow or suspended bed upflow units. Packed bed downflow carbon columns are generally operated under pressure.

This report details the evaluation of tertiary treatment of a conventional secondary effluent (step-aeration) pilot scale process to produce an effluent with low phosphorus, and particulate organic and inorganic concentrations that meet the requirements for discharge to the Potomac River. The tertiary system consisted of lime precipitation (two-stage with intermediate recarbonation or single-stage with sodium carbonate addition), ammonia stripping, dual media filtration, neutralization and activated carbon adsorption. Ammonia stripping was applied only during portions of the study to determine the effect of temperature on ammonia removal and the calcium carbonate scale rate at pH 10.5.

SECTION II

CONCLUSIONS

Two stage lime precipitation of a good quality (suspended solids less than 25 mg/l) step aeration effluent produced low phosphorus and BOD residuals of 0.13 mg/l and 2.1 mg/l respectively.

Dual media filtration of the chemically clarified effluent reduced phosphorus and BOD concentrations to 0.09 mg/l P and 1.4 mg/l, respectively.

Activated carbon adsorption removed 55 percent of the total organic carbon from the neutralized filter effluent. This removal resulted in an average residual TOC of 3.7 mg/l.

Single stage clarification (pH 11.5, sodium carbonate addition) with a good quality secondary effluent produced a phosphorus residual of 0.53 mg/l as P in the clarified effluent. The carryover precipitated phosphorus, however, was filterable as filtration produced an effluent with an average residual phosphorus concentration of 0.10 mg/l P.

Operational difficulties in pumping the sodium carbonate solution produced a carryover of excess soluble calcium ion into the filter. The post precipitation of these ions as $CaCO_3$ in the filters caused cementation of the media and channeling in the filter.

Recalcined lime, with recoveries up to 75 percent of the total solids slurry, was recycled to the clarification system without a loss in efficiency of the tertiary system.

Filamentous growths in the activated sludge system caused high organic solids concentrations to enter the first-stage clarifier, this produced slurry pool instability and reduced the efficiency of the system.

At inlet water and air temperatures 25.0 and 24.4°C (77°F and 76°F), respectively, and an air to liquid rate of 2.45 M^3 air/liter water (327 ft^3 air/gallon liquid), 80 percent of the available ammonia was stripped from the effluent of the two-stage lime system at ph 10.5. A reduction in inlet air temperature to 6°C (43°F) reduced the removal efficiency by 30 percent. At pH 10.5, the calcium carbonate scale rate was 16 mg/l $CaCO_3$.

SECTION III

RECOMMENDATIONS

Tertiary treatment has demonstrated high removals of phosphorus and organic carbon. Future work in tertiary treatment should be related to nitrogen removal since air stripping of ammonia is too restrictive because of air temperature effects. Breakpoint chlorination and selective ion exchange are alternative ammonia processes and should be demonstrated in tertiary applications.

The use of sodium carbonate in conjunction with the high lime process should be studied to determine the kinetic rates of reaction. The kinetic rate of reaction of the lime and carbon dioxide should be determined to provide better design criteria.

The two-stage lime system, although producing excellent quality of water, produces a large amount of solids. Alternatives, such as low lime pH treatment with ferric chloride should be investigated.

SECTION IV

EXPERIMENTAL

Pilot System

The system for the tertiary treatment of the effluent from a 265 liters/min (70 GPM) step aeration pilot plant is shown in Figure 1. The two clarification units (solid contactors) were identical in design with a side wall depth of 2.9 m (9.5 ft.) (Figure 2). Each clarifier was divided into 4 zones; a primary mixing zone (rapid mix), a secondary mixing zone (flocculation), a clarification zone and a sludge densification zone. The clearance between the bottom (discharge) of the secondary mixing zone and the flat bottom of the clarifier was .91 meters (3 ft.). Solids from the densification zone were externally recycled at 10 percent of average flow to the primary mixing zone to increase the rate of precipitation and produce particles of increased size and weight during flocculation. The variable speed turbine mixer in the primary and secondary mixing zones were operated at 36 and 15 rpm, respectively.

The clarification units were designed for a maximum flow of 378 m^3/d (100,000 gpd) with a maximum overflow rate of 81.5 m/d (200 gpd/ft^2). The system was operated on a diurnal cycle with the minimum, average, and maximum flows shown in Table 1 along with other operating bath. At an average flow of .15 liter/min (40 GPM) the clarification system treated 218 m^3/day (57,600 gpd) at an overflow rate of 45.6 m/d (1120 gpd/ft^2).

During the two-stage operation, the pH was reduced to approximately 10.5 in the recarbonation tank where the average contact time was 15 minutes and a turbine mixer rotating at 75 rpm provided mixing.

Solids from the second clarifier were recycled to the recarbonation tank at 10 percent of the average flow. Five mg/l of Ferric ions were added to the primary mixing zone of the second clarifier to improve the flocculation of the precipitated column carbonate.

Single-stage operation consisted of pumping sodium carbonate solution to either the primary or secondary mixing zone of the first clarifier to precipitate the excess column ions. The recarbonation tank and second-stage clarifier were eliminated.

During both the single and two-stage operation, solids were wasted at approximately 2 percent of average inlet flow from the first-stage clarifier. Solids were wasted at similar rates from the second clarifier to the first clarifier during the two-stage operation.

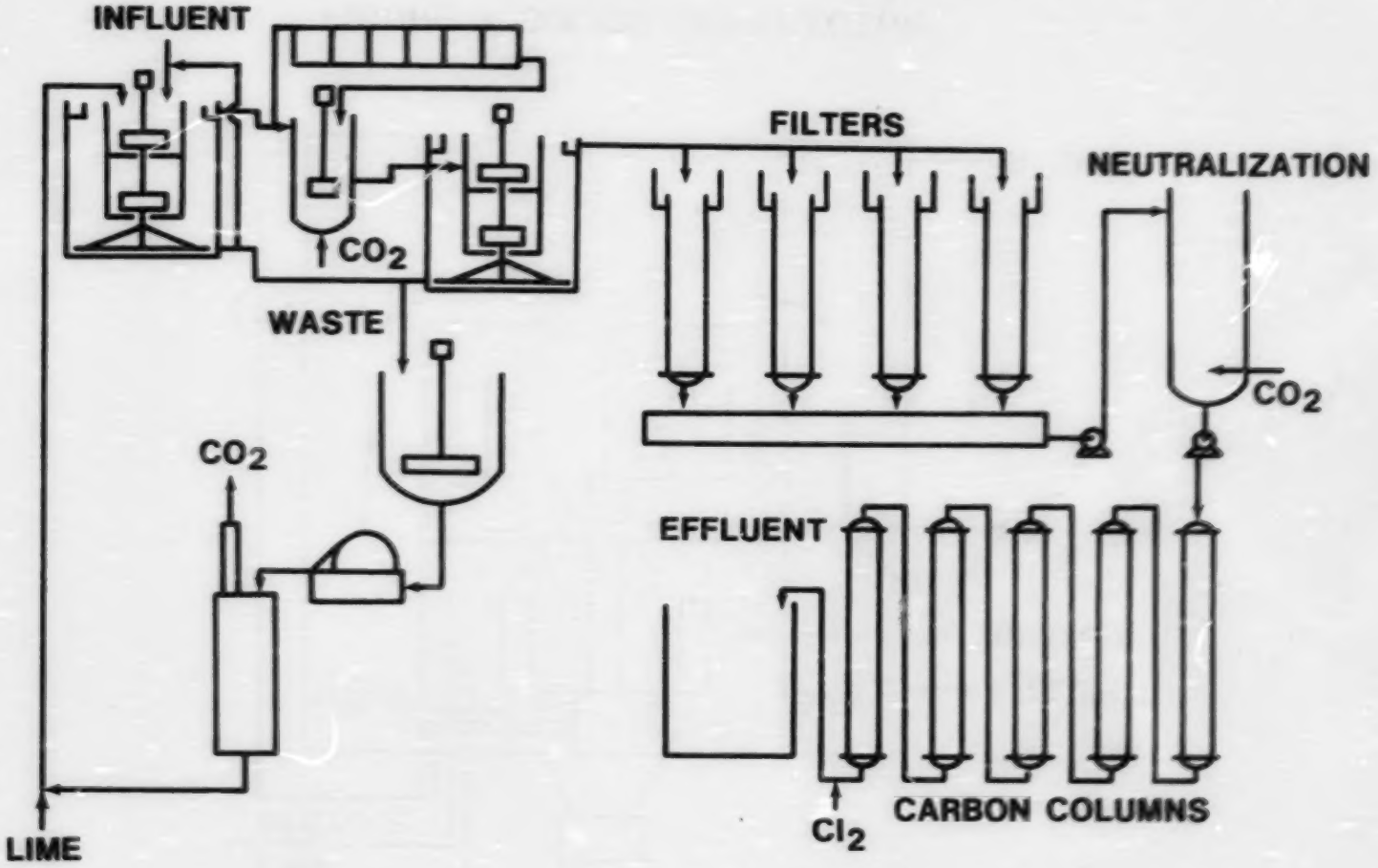

FIGURE 1. TERTIARY PILOT PLANT SYSTEM

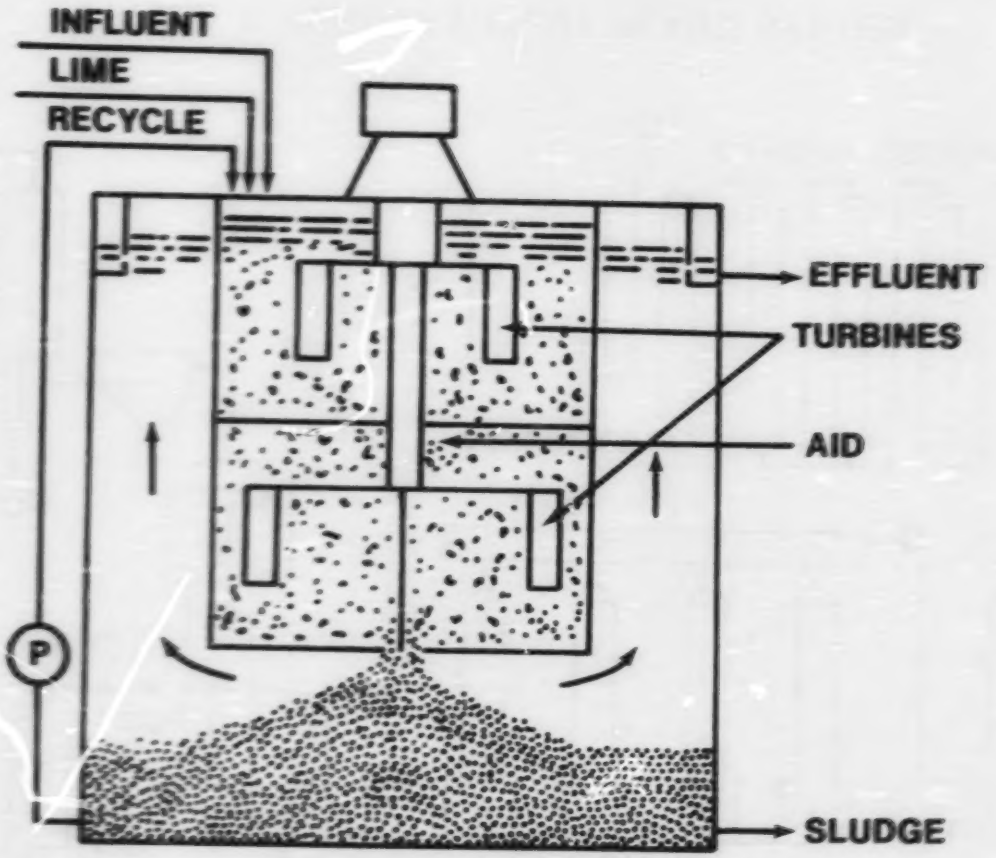

FIGURE 2. SOLIDS CONTRACTOR

TABLE 1. TERTIARY OPERATING CONDITIONS

	Flow Rate liter/gal	Loading	Detention Time minutes
Lime Precipitation			
Stage 1 and 2	87 min	26.1 m/d	
	151 ave	45.6 m/d	154
	204 max	61.5 m/d	
	265 rain peak	79.4 m/d	
Recarbonation	151 ave		15
Primary Zone	151 ave		14
Secondary Zone	151		20
Air Stripping			
5 Towers	121 constant	.0815 m/min	
Filtration			
2 Filters	87 min	.0803 m/min	
	151 ave	.139 m/min	
	204 max	.188 m/min	
	265 rain peak	.244 m/min	
Carbon Adsorption			
4 Columns	1.21 constant	.285 m/min	30

Ammonia air stripping was applied to the second-stage clarifier effluent at pH 10.5. The stripping system (Figure 3) included five crossflow cooling towers each packed with forty 1.2 m by 1.5 m by 1.3 cm (4 ft by 5 ft by 0.5 in.) polypropylene grids. The layers of each grid were spaced every 6.4 cm (2.5 in.) and the grids were packed to promote waxed air flow through the system. The water was pumped to a distribution box located on the top of each tower and flowed downward over the grids. The air was drawn countercurrent to the flow of water between towers and crossflow to the water flow within the packing of each tower by 3.7 Kw (5 hp) centrifugal fan.

The effluent from the first stage clarifier during the single-stage operation and the effluent from the second-stage clarifier during the two-stage operation were fed to the filtration system. The filtration system consisted of a splitter box followed by two gravity fed dual-media filters (3.0 m [10 ft.] of hydraulic head). Each filter was packed with 46 cm (18 in.) of 0.9 mm anthracite coal on 15 cm (6 in.) of 0.45 mm sand. Fused aluminum oxide plates were used to support the media and provide flow distribution during backwash. The filters were backwashed for 10 minutes by a sequential surface wash-backwash system. The flows of the surface wash and backwash systems were 0.12 and 0.81 m/min (3 and 20 gal/min/ft^2), respectively.

A side stream of the filtered effluent was neutralized to pH 7-8 and pumped through the activated carbon adsorption system. The system included four 7.6 cm (3-inch) columns packed to a depth of 2.1 m (7 feet) per column with 8 x 30 mesh Calgon activated carbon. At a constant rate of 1.2 liters/min (0.32 gal/min) the loading to the column was 0.285 m/min (7 gal/min/ft^2) with a total empty bed contact time of 30 minutes. The columns were manually backwashed every day at a rate of .61 m/min (15 gpm/ft^2).

Analytical Procedures

The system operated 24-hours a day, 7 days a week, with samples taken every four hours and composited for 24 or 48 hours, depending on the nature of the sample. Samples were stored at 3°C to minimize biological activity. Effluent samples were analyzed for TOC, BOD, COD, total phosphorus, TKN, ammonia, calcium, magnesium and total solids.

Total organic carbon was determined by the Beckman Carbonaceous Analyzer (11); and the 5-day BOD, by the probe method (12). Calcium and magnesium concentration were determined by the Perkin and Elmer Model 303 Atomic Adsorption Unit (12). Ammonia (12), nitrite and nitrate (13) were determined on a Technicon Autoanalyzer. Total phosphorus was measured by the persulfate method (14) and the methods for all other analyses were taken from "Standard Methods" (15).

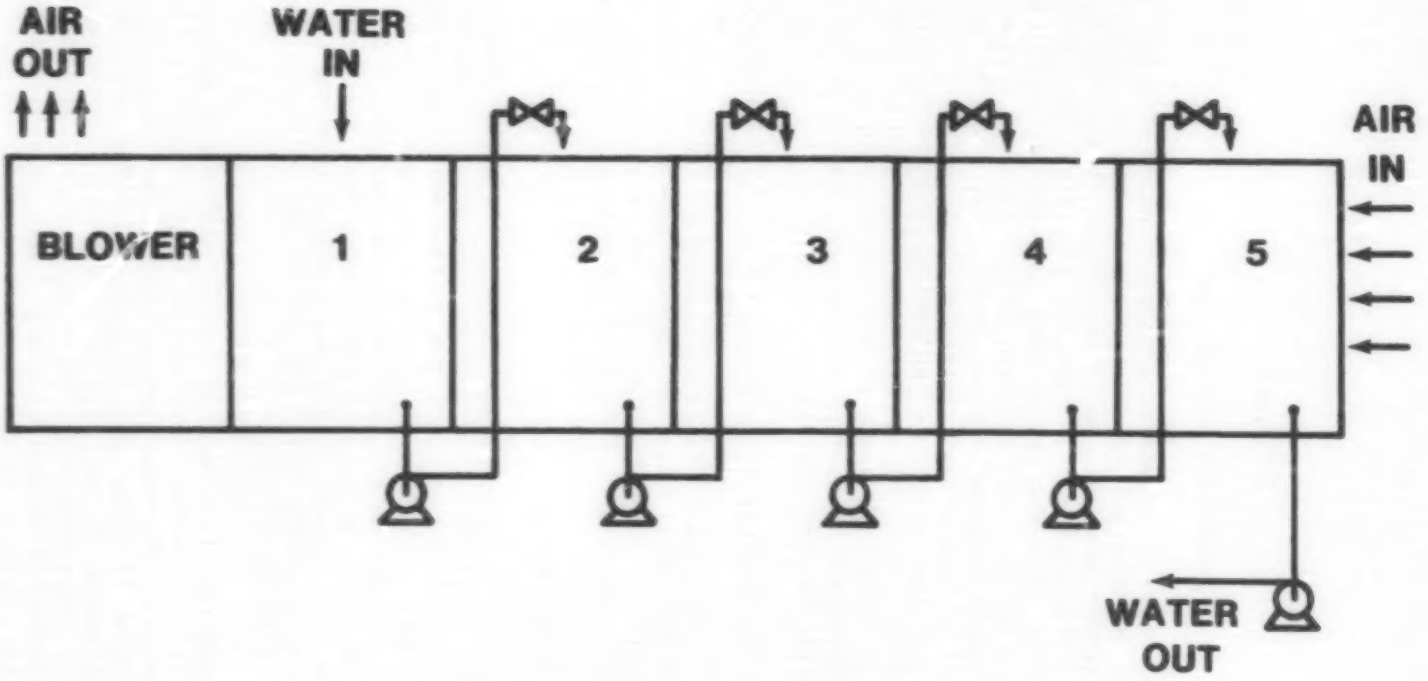

FIGURE 3. AMMONIA AIR STRIPPING SYSTEM

SECTION V

OPERATION AND RESULTS

On February 9, 1970, tertiary treatment of the secondary effluent from the Pilot Plant step aeration process was initiated with the start-up of the lime precipitation process. Dual media filtration of the chemically clarified secondary effluent began on February 27, 1970. The clarification system was operated in two stages with intermediate recarbonation at a constant rate of 40 GPM until June 18, 1970. Then the system was placed on a 2.3:1 diurnal flow variation. On July 23, 1970, a single stage lime clarification with sodium carbonate was substituted for the two-stage lime clarification with intermediate recarbonation, and operated until December 23, 1970. The effluent from the second-stage clarifier was pumped to the air stripping system from March 24, 1970 until July 14, 1970. The carbon adsorption system was placed in operation on April 16, 1970 and operated until October 13, 1970.

Process flows with corresponding hydraulic loadings and detention times are summarized in Table 1; the operating variables in Table 2. As seen in Table 2, the nitric acid produced by nitrification in the step aeration process during the summer months reacted with the alkalinity and lowered the buffer capacity of the secondary effluent. In addition, the conversion of ammonia to nitrate restricted the operation of the air stripping system.

Clarification and Filtration

During the study, four alternate methods controlled the lime feed: conductivity control, alkalinity-flow proportional control (Calgon Chemonitor), pH-flow proportional control and fixed dose-flow proportional. The pH-flow proportional control system provided the most reliable operation (16). The apparent increase in the lime dose shown in Table 2 for the month of June and later was caused by recycling the recalcined lime into the clarification system. The recycled lime was obtained from the lime sludge which was dewatered on a vacuum filter and recalcined (17) with the non-carbonate (inert) solids in the cake.

During two stage operation, five mg/l of ferric ions were added to the primary mixing zone of the second clarifier to improve the flocculation of the calcium carbonate. The waste solids from the second clarifier were pumped to the first clarifier with wasting of solids from the total system through the blowdown of the first clarifier. The waste rate from the first clarifier at approximately 1.5 percent of total flow produced a total solids concentration of approximately 5 percent in the blowdown and maintained a solids balance in the system.

TABLE 2. OPERATING VARIABLES

Month	Alkalinity mg/l $CaCO_3$	Lime Dose mg/l CaO	1st Stage pH	2nd Stage pH	Na_2CO_3 mg/l	1st Stage Waste % of influent	2nd Stage Waste % of influent
March	117	390	11.8	10.4		1.59	3.50
April	79	330	11.8	10.3		1.46	3.24
May	79	353	11.8	10.3		1.47	2.36
June	54	450	11.7	10.2		1.06	2.16
July	70	466	11.5	10.3		1.49	
August	84	342	11.7		273	2.09	
September	115	542	11.7		271	2.06	
October	144	546	11.6		272	2.20	
November	146	430	11.6		194	1.54	
December	143	409	11.5		210	1.10	

In the two-stage operation, the recycle of solids from the second clarifier to the first clarifier and the relatively low amount of organic solids in the step aeration effluent produced slurry pool stability in the clarifiers. Initiation of the diurnal cycle with a dry weather peak overflow rate of 61 m/d (1,500 gal/day/ft^2) did not decrease the process removal efficiencies or the slurry pool stability in either clarifier. In addition, the use of recalcined lime with recycled inerts in June and July did not alter the process removal efficiencies.

The efficiencies of removal of phosphorus, BOD, TOC, COD, and suspended solids by lime precipitation are summarized in Tables 3, 4 and 5. Two-stage lime precipitation and filtration, operated until July 23, 1970 on high quality secondary effluent from the step aeration process, produced excellent removals of BOD and phosphorus. The average residual phosphorus concentrations following clarification and filtration were 0.13 and 0.09 mg/l as P, respectively. The efficient step aeration process converted the soluble BOD materials to insoluble particulates which were captured in the tertiary chemical clarification and filtration systems. After two-stage lime clarification and filtration, the average residual BOD's were 2.1 and 1.4 mg/l, respectively. The phosphorus and BOD residuals after filtration corresponded to an accumulated removal from the raw wastewater of approximately 99 percent. The average residual TOC and COD after clarification were 9.1 and 18.4 mg/l respectively, and after filtration were 7.5 and 17.5 mg/l. The average residual suspended solids concentrations in the clarified and filtered effluents were 17.3 and 3.8 mg/l.

Single-stage lime clarification at pH 11.5 with sodium carbonate addition and filtration was operated from late July to late December. The operation included a period of seasonal change in water temperature. In single stage lime precipitation, sodium carbonate was added to the secondary mixing zone of the first clarifier to precipitate the excess calcium ions. The effluent from the first-stage clarifier was fed directly to the filters, by-passing the recarbonation tank and the second clarifier. During the first three months of operation, the waste rate was maintained at approximately 2 percent of influent flow and produced a solids concentration in the bottom of the clarifier of approximately 3.5 percent. Later, the waste rate was gradually reduced to approximately 1 percent to increase the solids concentration in the blowdown. As a result of this change in wasting rate, the solids in the sludge blowdown increased to greater than 5 percent. The single stage system test was interrupted during late October when filamentous organic solids from the upstream step aeration process overflowed the secondary weirs into the lime clarification process and caused instability of the slurry pool in the lime clarifier.

TABLE 3. PHOSPHORUS REMOVAL FOR SINGLE AND TWO-STAGE LIME PRECIPITATION OF SECONDARY EFFLUENT*

Month (1970)	Influent mg/l	Clarification		Filtration	
		mg/l	% Removal	mg/l	% Removal
March	6.2	0.11	98	0.11	98
April	6.1	0.13	98	0.10	98
May	6.4	0.11	98	0.06	99
June	6.8	0.16	98	0.11	98
July	7.2	0.14	98	0.09	99
August	6.7	0.41	94	0.08	99
September	6.7	0.72	89	0.07	99
October	7.1	0.46	93	0.16	98
November	7.3	0.59	92	0.36	95
December	6.6	0.59	91	0.29	96

*Phosphorus concentrations reported as P

TABLE 4. BOD REMOVAL FOR SINGLE AND TWO-STAGE LIME PRECIPITATION OF SECONDARY EFFLUENT

Month (1970)	Influent mg/l	Clarification mg/l	Clarification % Removal	Filtration mg/l	Filtration % Removal
March	10.4	1.9	82	1.6	85
April	12.1	2.5	79	1.6	87
May	10.2	2.7	74	1.3	87
June	20.7	1.6	92	1.3	94
July	20.5	1.8	91	1.3	94
August	17.6	1.8	89	1.5	91
September	10.7	2.1	80	1.8	83
October	29.8	4.4	85	3.5	88
November	31.8	13.0	59	8.3	74
December	33.0	10.4	68	10.5	68

TABLE 5. TOC, COD AND SUSPENDED SOLIDS REMOVAL FOR SINGLE AND TWO-STAGE LIME PRECIPITATION OF SECONDARY EFFLUENT

	TOC mg/l	% REMOVAL	COD mg/l	% REMOVAL	SUSPENDED SOLIDS mg/l	% REMOVAL
Influent						
Two-Stage*	19.2	---	48.6	---	33	---
Single-Stage**	23.0	---	69.7	---	34	---
Clarification						
Two-Stage*	8.1	58	18.4	62	17.3	48
Single-Stage**	11.9	48	27.0	61	16.3	52
Filtration						
Two-Stage*	7.5	61	17.4	64	3.8	89
Single-Stage**	11.2	51	26.0	63		77

* March - July, 1970
** August - December, 1970

As seen in Table 3, the conversion of the two-stage system to single stage produced an increase in the residual phosphorous concentration following clarification. However, during the first three months of operation, filtration successfully moved the precipitated phosphorus to an average residual of 0.10 mg/l as P.

During the first three months of single stage operation, the residual BOD following clarification and filtration averaged 2.6 and 2.3 mg/l, respectively (Table 4). The TOC and COD concentrations after filtration averaged 9.1 and 21.2 mg/l, respectively, during the first three months of single stage operation and represented a slight increase as compared to the two-stage system. An increase in the filtered effluent suspended solids concentration from 3.8 mg/l during the two-stage operation to 6.2 mg/l during the first three months of the single-stage operation may be caused by the use of the recycled lime or the lack of the ferric chloride addition within the single-stage system. The low phosphorus concentration of 0.10 mg/l as P for the first three months of operation indicates that the increased suspended solids concentrations did not contain calcium hydroxylapatite. The average TOC, COD and suspended solids concentrations after single stage clarification and filtration as shown in Table 5 for the full five months (Aug.-Dec.) were moderately higher than those of the two stage operation and reflected sludge bulking conditions in the upstream biological (step aeration) process during November and December.

A solids balance for the month of October on the chemical clarification system is shown in Table 6. The balance was performed with recalcined lime equal to 74 percent of the total weight of slurried solids added to the system to maintain a pH of 11.6. The solids production was based on the average phosphorus, calcium, magnesium and suspended solids concentrations in the influent and effluent to the clarifier. The excess calcium was assumed to be calcium carbonate. The solids in the recycle lime were calculated from average concentrations of Ca^{++}, Mg^{++} and phosphorus in the recalcined lime. The magnesium in the recycled solids was assumed to be insoluble MgO. With these assumptions, the total solids production was calculated to be 0.80 kg/m^3 (6.7 lbs/1000 gal). Based on the total waste flow and the average total solids of the waste flow, the measured total solids production of 0.86 kg/m^3 (7.1 lbs/1000 gal) was within 5.6 percent of the calculated solids production.

When water temperatures began to sharply decrease in late October, the step aeration process developed filamentous sludge, and the conversion of the soluble BOD to particulate BOD gradually decreased. The filamentous sludge with its poor settling characteristics produced bulking sludge which overflowed the weirs of the secondary settler into the tertiary chemical clarification system. Thus the amounts of organic materials (BOD, TOC, and COD) increased in the secondary effluent (Tables 4 and 5). Although the lime system clarified the secondary effluent during the final two months of operation (the clarified effluent suspended solids concentration averaged 13.5 mg/l), the BOD following clarification increased to 11.7 mg/l. Likewise

TABLE 6. SOLIDS BALANCE DATA FOR SECONDARY EFFLUENT OPERATION (OCTOBER 1970)

	Production kg/month	Recycled kg/month	Total kg/month
$Ca_5(OH)(PO_4)_3$	236	572	807
$CaCO_3$	3538	305	3538
$Mg(OH)_2$-MgO	139	305	444
Suspended Solids	249		249
Unknowns	____	191	191
	4162	1068	5230

Volume of wastewater in October: $6567 m^3$

Measured solids production: 5265 kg

Solids production per unit volume:

Calculated $\frac{5230 \text{ kg}}{6567 \text{ m}^3} = .80 \text{ kg/m}^3$ (6.7 lb/1,000 gal)

Measure $\frac{5265}{6567} = .86 \text{ kg/m}^3$ (7.1 lb/1,000 gal)

* Calculated from measured concentrations of Ca^{++}, PO_4, Mg^{++} and suspended solids and stoichiometry of precipitation reactions. Calculation assumes complete calcination of $CaCO_2$.

** Based upon complete measured values of total solids concentration and volume of waste solids slurry.

the TOC and COD following chemical clarification increased to 15.1 and 34.9 mg/l, respectively. With the increase in biological solids in the clarifier, the TOC of the wasted solids also doubled and slurry pool instability occurred.

The decrease in water temperature also disrupted pumping of the sodium carbonate and as a result adversely affected the filtration process. Soda ash crystallization in the pump and associated piping prevented uniform addition of sufficient sodium carbonate. As a result, calcium ion concentrations in the clarified effluent increased from approximately 40 mg/l to 70 mg/l. The excess clacium ions post-precipitated as $CaCO_3$ in the filters and converted the filter media to solids chunks within a month. Channeling of the filters occurred, reducing filter efficiency. Backwashing the filter was ineffective and filter runs decreased from the normal 50 to 10 hrs. This poor filtration produced an increase in phosphorus concentration following filtration from the normal 0.1 mg/l to an average of 0.33 mg/l as P and in suspended solids concentration from the normal 6 mg/l to 10.3 mg/l.

Ammonia Air Stripping

During the operation of the ammonia stripping process, the entire tertiary treatment system was operated at a constant rate of 32 gpm. The loading to the air stripping system was .081 m/min_3 (2 gpm/ft^2) with an initial G'/L' value of approximately 2600 m^3 air/m^3 liquid (350 cu. ft air/gal liquid).

The step aeration process fluctuated through various stages of nitrification and thus, after chemical clarification, provided an influent to the ammonia stripping column of varying ammonia concentration (Figure 4). During the first 17 days of operation (Figure 4), nitrification did not occur in the step aeration process. The average concentration of ammonia in the inlet and outlet of the tower were 9.5 and 4.2 mg/l NH_3-N, respectively, for an average removal of 56 percent. During this period, the average outlet water temperature was 7.2°C (45°F) with an average G'/L' value of 2600 m^3 air/m^3 liquid(347 cu ft air/gal liquid). Between the 35th and 45th days of operation, the step aeration system produced little nitrification, and the percent removal of ammonia averaged 66 percent (3.1 mg/l NH_3-N average residual) with an average outlet water temperature of 13.9°C (57°F). During previous studies (7), nearly 80 percent of the ammonia was removed under similar operating conditions with an outlet water temperature of 20.5°C (57°F).

While stripping efficiencies were affected by temperature, the rate of calcium carbonate scaling and its effect on the reduction in the air-to-liquid ratio were significantly affected at pH 10.5. The calcium carbonate scale in the pH 10.5 tests reduced the air-to-liquid

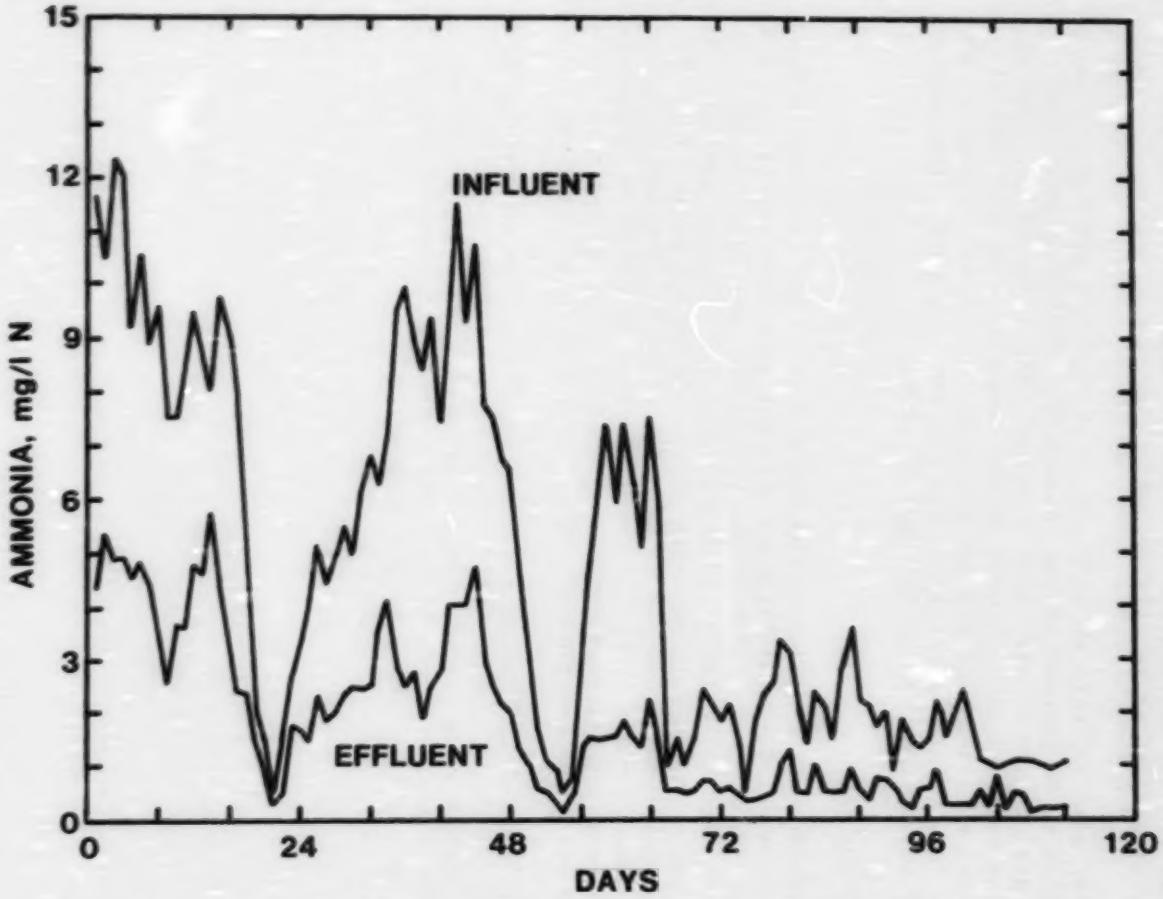

FIGURE 4. AMMONIA CONCENTRATION AS AFFECTED BY BIOLOGICAL NITRIFICATION

ratio from an initial 260 m^3 air/m^3 liquid (350 cu ft air/gal liquid) to approximately 330 cu ft air/gal liquid (Figure 5) over the 112 day period. During the operation with the effluent at pH 10.5, inlet and outlet calcium ion concentrations averaged 48.3 and 41.8 mg/l of Ca^{++}, respectively. The calcium ion decrease corresponded to a calcium carbonate scaling rate of 16 mg/l of $CaCO_3$.

In earlier work (7) with an influent pH of 11.5 and air temperature of (78°F) 25.6°C, 90 percent of the ammonia was removed at an air to liquid rate of 3.75 m^3 air/liter of water (500 cu ft air/gal liquid). In similar tests at pH 11.5 with an air temperature of 6°C (43°F) the removal efficiency of the air stripping system was reduced to 60 percent. At an inlet pH of 11.5, the calcium carbonate scale rate on the packing was found to be 125 mg/l of $CaCO_3$.

Carbon Adsorption

The small carbon adsorption system was fed lime clarified neutralized (carbon dioxide addition) filtered effluent at a constant rate of 1.21 liter/min (0.32 gpm). The 4 column system was operated from April 16 through October 13, chiefly to demonstrate final product quality. Although a daily backwash schedule was maintained, biological activity in the last month of operation within the columns increased the pressure drop across the adsorption system. The differential pressure losses exceeded the head capacity of the small positive displacement and during the final 30 days of operation a reduced flow of .91 liter/min (0.24 gal/min) was maintained.

The efficiency of the system for total organic carbon removal is shown in Table 7. The effluent TOC increased from 2.4 mg/l to 4.8 mg/l with a corresponding percent removal decrease from 65 to 49 percent during the 6 months of operation. The estimated loading on the two lead columns was 0.12 kg TOC/kg carbon applied.

TABLE 7. TOC REMOVAL BY ACTIVATED CARBON ADSORPTION

Month (1970)	Influent mg/l	Effluent mg/l	Removal %
April*	6.9	2.4	65
May	7.7	2.9	62
June	7.5	3.1	59
July	7.7	3.5	55
August	9.9	4.5	55
September	7.8	4.9	37
October**	9.5	4.8	49

* April 16-30

** October 1-13

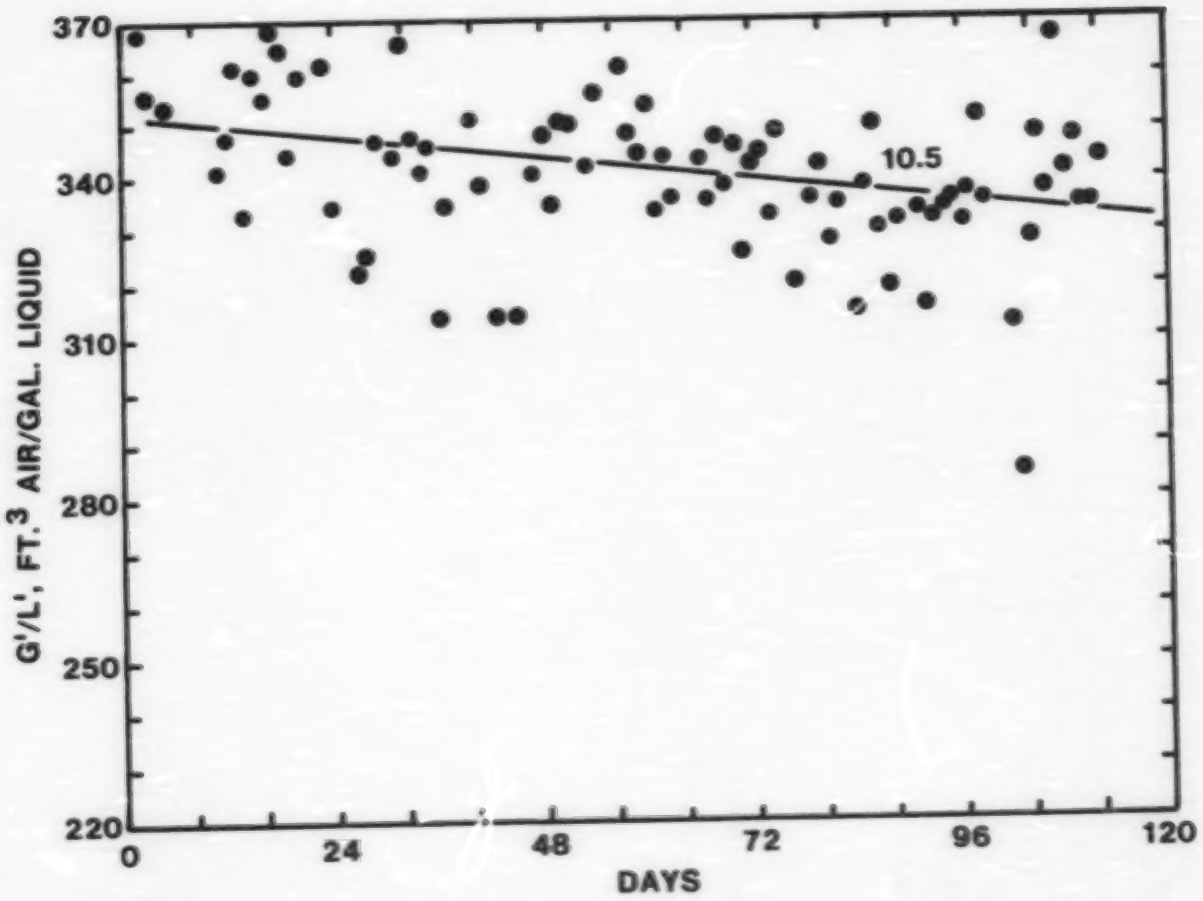

FIGURE 5. CALCIUM CARBONATE SCALE AFFECT ON AIR FLOW RATE

SECTION VI

OVERALL SYSTEM PERFORMANCE

The operation of a tertiary treatment system on a good quality secondary effluent has demonstrated that a high quality effluent is possible. The results of the operation which included two-stage lime precipitation, air stripping of ammonia, dual-media filtration and activated carbon adsorption are presented in Table 8. The nitrogen residual, which includes ammonia and organic nitrogen, was attained only during warm temperatures (24°C [75°F]). To meet the Potomac River discharge requirement, breakpoint chlorination (10) of the residual nitrogen could be used for additional ammonia removal and would reduce the final nitrogen level to approximately 2 mg/l.

TABLE 8. TERTIARY SYSTEM PERFORMANCE

	TOC mg/l	Phosphorus mg/l	Nitrogen mg/l
Raw	104	8.4	22
Secondary	19.2	6.4	17
Clarification	8.1	0.13	15
Air Stripping*	---	---	5.0
Filtration	7.5	0.09	---
Carbon Adsorption	3.7	---	---

*Air Stripping represents studies at inlet air temperatures of 76°F (24.4°C).

SECTION VII

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SECTION VIII

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